(9) Because our original sample of optically active **3** is now recognized to have been impure,[1] the racemization data reported earlier[4e] is in error and should not be considered relevant.

(10) Anet and Bock[4a] observed that the diasterotopic methyl signals which appear at δ 1.73 and 1.62 (60 MHz) coalesce at 70 °C. Through use of the formula $k_{\mathrm{coal}} = \pi\Delta\nu/\sqrt{2}$ to approximate the rate constant for ring inversion and substitution of this value into the Eyring equation,[8] we have obtained the $\Delta G^{\ddagger}{}_{\mathrm{RI}(70°)}$ value cited in Table V.

(11) Meisinger, R. H. Ph.D. Thesis, The Ohio State University, 1973.

(12) The nonregularity of the increments can be attributed to the operation of buttressing effects in the tetrasubstituted examples. The magnitude of the buttressing compares amazinlgy well with that observed in sterically crowded phenanthrenes: Frish, M. A.; Barker, C.; Margrave, J. L.; Newman, M. S. *J. Am. Chem. Soc.* **1963,** *85*, 2356; Karnes, H. A.; Kybett, B. D.; Wilson, M. H.; Margrave, J. L.; Newman, M. S. *ibid.* **1965,** *87*, 5554.

(13) The same conclusion has recently been arrived at independently (in less explicit form) by H. Baumann: *J. Am. Chem. Soc.* **1978,** *100*, 7196.

(14) This investigation was supported in part by the National Cancer Institute, DHEW (grant No. CA-12115), the National Science Foundation (Grant No. CHE7608764), the Deutsche Forchungsgemeinschaft, and the Fonds der Chemischen Industrie. Enlightening exchanges of information were had with Professors Jack Hine and Gerhard Binsch.

(15) The Ohio State University Dissertation Fellow, 1977–1978.

John M. Gardlik,[15] Leo A. Paquette*
Evans Chemical Laboratories, The Ohio State University
Columbus, Ohio 43120

Rolf Gleiter*
Institut für Organische Chemie der Technischen Hochschule
D61 Darmstadt, West Germany

Received December 14, 1978

Configuration and Planarity of Fluorescent and Nonfluorescent 1,5-Diazabicyclo[3.3.0]octadienediones (9,10-Dioxabimanes) by X-ray Crystallography

Sir:

We have recently described the synthesis and some properties of an essentially new class of compounds, the 1,5-diazabicyclo[3.3.0]octadienediones (briefly, 9,10-dioxabimanes or "bimanes").[1] We now confirm that strongly fluorescent bimanes are syn isomers and weakly fluorescent bimanes are anti isomers (see formulas below). We further report that some *syn*- and *anti*-bimanes are planar and that others are nonplanar, including an unusual dicyanomethylene bridged bimane. These facts are established by X-ray crystallography from data recorded on a four-circle diffractometer with structures solved by direct methods. There is no obvious relationship between the planarity and the photophysical properties as will be described in more detail elsewhere.[2]

Single crystals of the strongly fluorescent (C_6H_5,Cl)B isomer were grown from acetonitrile solution. The crystal data are $a = 6.822$ Å, $b = 10.614$ Å, $c = 11.589$ Å, $\alpha = 100.79°$, $\beta = 81.98°$, $\gamma = 102.16°$, space group $P\bar{1}$, and $Z = 2$. An anisotropic least-squares refinement of the structural model converged to $R = 0.069$. The structure reveals a diazabicyclooctanedione system with both carbonyl groups on the same side: a *syn*-bimane. The central part of the molecule is slightly bent about the N–N bond, the dihedral angle between the adjacent five-atom rings being 171.6°. The crystal packing seems to be affected by strong dipolar interactions between molecules related to each other by the inversion center with overlap and interplanar distance closely resembling those for heteromolecular π complexes (Figure 1). The shortest interatomic contact between the overlapping moieties is the N···N distance of 3.18 Å. The distances of the atoms in one diazabicyclooctane unit from the mean plane of the framework of the second unit are in the range of 3.22–3.50 Å and average 3.34 Å. (Fluorescent (CH_3,H)B has a "π-complex" syn structure similar to that of the (C_6H_5,Cl)B described above.[3])

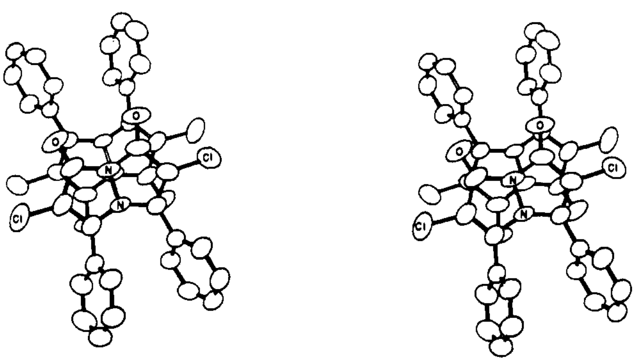
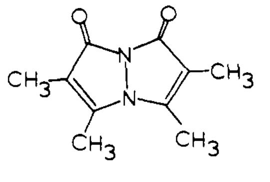


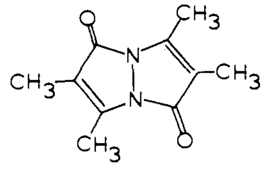
Figure 1. Computer generated (stereo-) drawing of *syn*-(C_6H_5,Cl)B (*syn*-"phenylchlorobimane") illustrating the close approach of pairs of molecules suggestive of π-complex formation.

The weakly fluorescent (C_6H_5,Cl)B crystallized from dichloromethane and diethyl ether in space group $P2_1/n$ and with $a = 9.942$ Å, $b = 16.132$ Å, $c = 10.529$ Å, $\beta = 110.88°$, $Z = 4$. The structure has been refined to $R = 0.050$. It shows an anti arrangement of the carbonyl groups and phenyl substituents with respect to the molecular framework. The diazabicyclooctane units deviate strongly from planarity, the dihedral angle around the central N–N bond being 147.3°.

The correspondence found between the molecular configuration and fluorescence for the "phenylchlorobimane" isomer pair also holds for the "methylmethylbimane" isomeric pair (formulas shown).



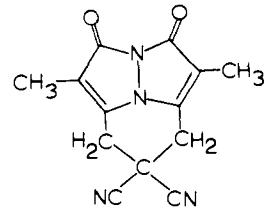
syn-(CH_3,CH_3)B
strongly fluorescent



anti-(CH_3,CH_3)B
weakly fluorescent

The data for crystals of the two "methylmethyl" bimanes follow: (a) *syn*-(CH_3,CH_3)B, $a = 6.608$ Å, $b = 6.043$ Å, $c = 13.300$ Å, $\beta = 113.71°$, space group Pc with $Z = 2$; (b) *anti*-(CH_3,CH_3)B, $a = 3.953$ Å, $b = 10.783$ Å, $c = 11.499$ Å, $\beta = 92.81°$, space group $P2_1/c$ with $Z = 2$. The tetramethyl substituted *anti*- and *syn*-diazabicyclooctadienone structures have been refined anisotropically to $R = 0.054$ and $R = 0.041$, respectively. The former is planar since it occupies a crystallographic inversion site of symmetry; the latter, occupying a general crystallographic position, is planar within experimental error. In the anti isomer, molecules are stacked along the a axis of the crystal unit cell, the separation perpendicular to the molecular plane being only 3.54 Å. For the syn isomer, the molecules are stacked along the b axis in two types of columns related by the glide plane. A "π-complex" arrangement is not present in the crystal; there is little overlap between adjacent units in the stack, and the corresponding perpendicular distance between molecular planes is also relatively large (3.65 Å). A single structure of an *anti*-bimane has previously been reported, but it is not sufficiently accurate to allow detailed comparison with our work.[4]

Crystal data for the bridged *syn*-bimane, the μ-[$(CN)_2$C]-*syn*-(CH_2,CH_3) (formula shown), follow: $a = 9.956$ Å, b



μ-($(CN)_2$C)-syn-(CH_2,CH_3)B

0002-7863/79/1501-1620$01.00/0

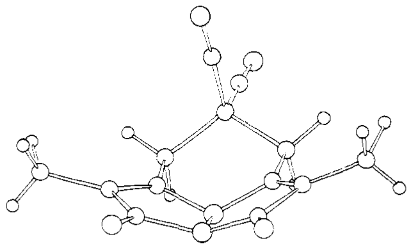


Figure 2. Structure of μ-((CN)$_2$C)-*syn*-(CH$_2$,CH$_3$)B (bridged "dicyanomethylene-*syn*-methylene, methylbimane").

$= 7.394$ Å, $c = 16.969$ Å, $\beta = 100.11°$, $P2_1/c$, $Z = 4$. Anisotropic refinement converged smoothly to $R = 0.047$.

Individual five-membered rings are not quite planar, and the two of them form a dihedral angle of 139.3°. The six-membered ring is in the chair conformation. Strain in the molecule is reflected in some of the bond angles and most notably in the long CH_2-$C(CN)_2$ bonds (1.568 Å). The structure is illustrated in Figure 2.

It is remarkable that the coplanarity of the two five-membered rings has little influence on the position or quantum yield of fluorescence. In dioxane, emission maxima and quantum yield for *syn*-(CH_3,CH_3)B and the bridged dicyano compound are 420 (0.72) and 426 nm (0.73), respectively. Substitution shifts the emission maximum for *syn*-(C_6H_5,Cl)B to 457 nm but affects the quantum yield only slightly (0.62). The implications of this combination of structural and photophysical information concerning the nature of the emitting state will be further examined.

References and Notes

(1) E. M. Kosower, B. Pazhenchevsky, and E. Hershkowitz, *J. Am. Chem. Soc.* 100, 6516 (1978).
(2) E. M. Kosower, H. Kanety, H. Dodiuk, and B. Pazhenchevsky, unpublished work.
(3) I. Goldberg, unpublished results.
(4) I. Søtofte, *Acta Chem. Scand.*, **27**, 661 (1973).
(5) (a) Tel-Aviv University; (b) State University of New York, Stony Brook; (c) 1977–1978, University of California, San Diego, LaJolla, Calif.; (d) J. S. Guggenheim Fellow, 1977–1978; (e) Ben-Gurion University of the Negev.

Edward M. Kosower,*[5a-d] Joel Bernstein*[5e]
Israel Goldberg,*[5a] Barak Pazhenchevsky,[5a] Ehud Goldstein[5e]
Department of Chemistry, Tel-Aviv University
Ramat-Aviv, Tel Aviv, Israel
Department of Chemistry, State University of New York
Stony Brook, New York 11794, and Department of Chemistry
Ben-Gurion University of the Negev, Beer-Sheva, Israel
Received August 18, 1978

Rigidity, Lipophilicity, and Henry's Constant

Sir:

Aranow and Witten[1] described a model for the influence of aliphatic chains on water solubility. In their model, solvent molecules interact with these chains, thus restricting internal rotation. Restriction is proportional to the energy of interaction and is thus much greater in water than in commonly applied organic solvents. Because of this interaction, there is much less gain of entropy when dissolving a compound in water than in most organic solvents.

Some applications of the model for physicochemical phenomena are given. We report two further applications of the model. When, owing to restricted internal rotation, solubility in water is lower than that in other solvents, it is obvious that compounds with a structurally restricted rotation will not display such a decrease in water solubility. This must also be reflected in their partition behavior.

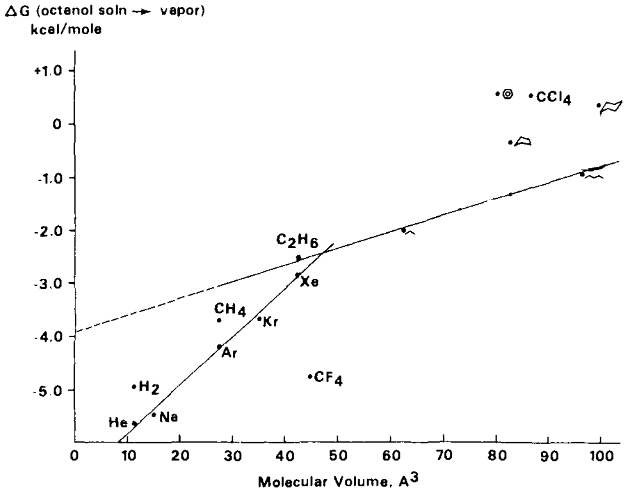


Figure 1.

Table I. Lipophilicity in Water/Octanol

compd	expt	calcd	diff
progesterone	3.87	5.61	1.74
11-deoxy-17-hydroxycorticosterone	2.46	3.52	1.06
deoxycorticosterone	2.88	4.52	1.64
testosterone	3.32	5.12	1.80
mean difference			1.56

The first application is concerned with lipophilicity. Lipophilicity is the decimal logarithm of the partition coefficient, and can be calculated by adding together the appropriate values assigned to the fragments of which the compounds are composed. These values are calculated from usually small, flexible compounds.[2] This means that, if the ideas of Aranow and Witten are correct, rigid molecules will have a lower experimental lipophilicity than calculated. This is well brought out by steroids, which possess an extremely rigid skeleton. Therefore, a few steroids were selected from the Hansch file, and their lipophilicity was calculated on the basis of Rekker's fragmental constants.[2] Table I compares the values obtained. The absence of restricted rotation provides a possible explanation of the difference in lipophilicity. If this explanation is correct, it would imply that (a) a rigidity factor should be included in the prediction systems for lipophilicity; (b) as this factor is entropy related and thus temperature dependent, the partition coefficient is also temperature dependent. Thus, if in a series of compounds the rigidity changes significantly, this would also have influence on the temperature dependence of the lipophilicity. Therefore, it is recommended that the partition coefficient at 310 K be measured if one wishes to correlate biological properties with lipophilicity. However, many other factors may be implicated, and even counterbalance one another. These include change of mutual solubility of the two solvents and changes in the degree of dissociation of the solute.

The second application lies in a related field, namely that of Henry's law, according to which the concentration of a solute and the pressure of its vapor have a constant as a quotient. This constant is a measure of the free energy necessary to bring a compound from the solvent to the vapor phase or vice versa.

Cramer[3] studied ΔG (solution–vapor) in relation to the molecular volume of the compounds. For water and octanol he obtained two separate plots, which are reproduced in Figures 1 and 2. From these figures it is readily apparent that all rigid molecules are on one line (for example, those of the noble gases, methane and benzene), while the flexible ones are on separate lines. The cycloalkanes occupy an intermediate position. This is in excellent agreement with the view that restricted rotation is an important factor. It can also be seen that

0002-7863/79/1501-1621$01.00/0